FIG. III—NITROGEN AS COTTONSEED MEAL

say that sulfate of ammonia should be sold cheaper than so-called high-grade nitrogen, because it comes from coal and that is cheap.

I believe the Fertilizer Industry has been, and is willing, to coöperate along any lines which will promote progress, and it seems to me that the Fertilizer Division of the American Chemical Society has a work along the line of availability of nitrogen which is well worth serious thought.

CARTERET, NEW JERSEY

THE DESTRUCTIVE DISTILLATION OF PACIFIC COAST KELPS

By D. R. HOAGLAND

Received April 6, 1915

The giant kelps of the Pacific Coast have received considerable attention in recent years, because of their high content of potash and iodine. The production of these substances from kelp on a commercial scale was first suggested by Balch[1] and the studies were later continued by the Bureau of Soils.[2] A more extended chemical investigation, however, seemed essential, and was undertaken by this laboratory. The principal results and conclusions of this work are reported elsewhere.[3]

In order to increase the margin of profit in the kelp industry, attempts have been made to find some method of utilizing the organic matter in addition to the potash and iodine. Among the suggestions, destructive distillation was considered. It is the purpose of this paper to report experiments dealing with this particular phase of our investigations.

Balch compared the distillation of kelp with that of beech wood and states that the volatile products from kelp—acetic acid, methyl alcohol and tar—"may be regarded as approximating in value those of beech wood." He assumes a value of $6.00 per ton of dry material for the volatile products of distillation. Green and Johnson[4] afterward made two distillations of 3-lb. samples of nereocystis and expressed the opinion that the distillates were worthless, but no analyses or details were given. Turrentine[1] distilled a 3-kg. sample of *Macrocystis pyrifera* in a Hornsy rotary still. An analysis of the gas evolved is given, but no data regarding the distillates. Further experimentation seemed necessary in order to make a more definite valuation of the volatile products.

FIG. IV—NITROGEN AS BASE GOODS

The distillations in this laboratory were conducted in an iron retort of about 1.5 gallons capacity. This was provided with a pyrometer and a suitable condenser. It is realized that distillation experiments on a small scale are not comparable with commercial practice, except to a limited extent. As a control, therefore, samples of oak and Douglas fir were distilled under identical conditions. It was hoped in this way to obtain a fair idea of the comparative value of the kelp. We believe such a comparison is permissible, especially since the yields of acid and alcohol for the oak and Douglas fir approximate those obtained in larger experiments on similar materials.[2] The methods of analysis were similar to those described by the U. S. Forest Products Laboratory.[3] The acetic acid was distilled with steam from a phosphoric acid solution.

Table I shows that the average yield of acetic acid was scarcely 0.2 that of Douglas fir and only 0.1 that of oak. The alcohol yields were in the same proportions. Tar oils to the extent of 4 to 7 per cent of the dry weight of the kelp separated out in the distillate. Most of the tarry material floats on the watery distillate. The tar oil analyzed as follows:

Sp. gr. at 17° C.	DISTILLATION FRACTIONS—PERCENTAGES			
	0 to 125° C.	125 to 250° C.	250 to 300° C.	Tar residue
0.984	11	27	23	39

The residue solidified to a hard, black, lustrous mass.

The kelp distillates were very slightly acid to litmus, but contained considerable amounts of basic substances. By the Kjeldahl method 3.2 g. of nitrogen were found in the total distillate from 1 kg. of dried kelp, approximately $^{1}/_{4}$ to $^{1}/_{5}$ of the total nitrogen contained in the material. It does not appear that ammonium compounds could be recovered from the liquors in commercially important quantities.

The gases evolved were not combustible during any of the early stages of the distillation, differing therein

---

[1] Balch, THIS JOURNAL, **1** (1909), 777.

[2] U. S. Senate Document, No. **190**.

[3] Burd-Calif. Exp. Station, *Bull.* **248**, and manuscripts in press by D. R. Hoagland and G. R. Stewart.

[4] Green and Johnson, *Chem. Eng.*, **15** (1912), 55.

[1] Turrentine, *Proc. Eighth Internat. Cong. Applied Chem.*, **15**, 313.

[2] Hawley and Palmer, *Proc. Eighth Internat. Cong. Applied Chem.*, **6**, 138; Benson, *Ibid.*, **25**, 331.

[3] Hawley and Palmer, *loc. cit.*

TABLE I—COMPARATIVE DISTILLATIONS OF KELP, DOUGLAS FIR AND OAK

	GRAMS OF MATERIALS OBTAINED						Total time of distillation Hrs.	% of dry wt. of material		
No. of run	Moisture	Distillate Total	Distillate Less moisture	Settled tar	Charcoal	Gas by diff.		Acid as acetic	Methyl alcohol 100%	Settled tar
ON 1 KG. OF KELP (*Macrocystis pyrifera*)										
3	116	290	174	..	465	245	3	..	..	..
6	116	255	139	..	465	280	2.5	..	..	..
9	116	265	149	..	500	235	12	..	..	..
11	116	262	146	48	485	253	3	0.34	Av. 0.14	5.4
12	116	283	167	41	512	205	3.75	0.49		4.6
13	116	277	161	60	472	251	4	0.28		6.8
14	116	242	126	37	487	271	4	0.28		4.2
15	116	217	101	30	515	268	8	..	..	3.4
23	116	277	161	60	485	238	4	0.49	0.20	6.8
24	116	305	189	55	460	235	8	0.58	0.18	6.2
ON 1 KG. OF DOUGLAS FIR										
16	190	414	224	60	260	326	3	1.5	0.7	7.0
17	190	424	234	80	276	300	2.5	..	0.7	10.0
25	190	450	260	100	300	250	4	1.6	..	12.0
ON 1 KG. OF OAK SAWDUST										
18	366	550	184	45	200	250	4	2.9	1.1	7.0
19	313	424	111	60	230	346	3.5	2.6	1.3	9.0
20	313	412	99	37	215	373	4.5	2.5	1.2	6.0

REMARKS ON DETAILS OF DISTILLATIONS

RUN NO. 3—Retort at red heat 1.5 hrs.
RUN NO. 6—Heated rapidly to red heat
RUN NO. 9—Very slow; low heat; 12 hrs.

RUN NO. 13
Started at 1.20 P.M.
Pyrometer readings
1.45 P.M. 120° C.
2.00 160
2.30 200
3.10 220
4.05 240
gases slightly combustible
4.30 360
gases burned steadily
4.50 420
5.10 500
no more distillate

RUN NO. 14—8.30 A.M.
9.15 A.M. 160° C. large watery distillate
9.30 200
10.35 220
11.15 280 gases slightly combustible
11.30 310 distillate oily gas burns
12.25 P.M. 500

RUN NO. 15—9.00 A.M.
9.30 A.M. 140° C.
9.50 170
10.45 190
12.00 M. 200
2.00 P.M. 220
2.15 290
3.20 390
4.30 400

RUN NO. 18—8.35 A.M.
Pyrometer readings
9.05 A.M. 170° C.
gases burn
9.15 200
10.05 270
11.50 290
12.30 P.M. 530

RUN NO. 20—1.05 P.M.
Pyrometer readings
1.40 P.M. 160° C.
2.40 200
3.20 250
5.25 500

RUN NO. 24—8.35 A.M.
Pyrometer readings
9.10 A.M. 160° C.
11.00 230
12.45 250
1.00 P.M. 300
2.45 440
4.45 530

from the gases produced by the oak and fir. Turrentine gives the following data regarding the gases evolved in his experiment:

ANALYSES OF GAS SAMPLES FROM DESTRUCTIVE DISTILLATION OF KELP (MACROCYSTIS)—(TURRENTINE)

Sample No.	1	3	5	7
Pyrometer	320° F.	480° F.	590° F.	900° F.
CO_2	80.0	70.0	44.0	20.2
Illuminants	2.0	4.0	10.0	3.3
O_2	0.5	1.5	0.8	0.5
CO	10.5	8.5	6.7	4.0
H_2	....	10.6	23.5	32.0
Methane	2.88	4.8	4.4	7.6
Nitrogen (by diff.)	4.12	0.6	10.6	32.4
Total per cent	100.00	100.00	100.00	100.00
Wt. per cu. ft.	0.106040	0.094	0.074150	0.057600
Cal. value	107.45	196.70	352.05	282.54

The charcoal residue was very soft and had a dull luster. A leaching experiment was made, using 2860 g. of charcoal, with an excess of distilled water. The solution was evaporated and three fractions crystallized out as is shown in Table II.

TABLE II—LEACHING AND FRACTIONATION

Fraction No.	Vol. of mother liquor	Wt. of dry salts Grams	Per cent of K_2O in salts	Per cent of I in salts	REMARKS
1	2600 cc.	450	58.0	0.03	Pure white crystals
2	1600 cc.	283	55.6	0.08	Nearly pure white crystals
3	860 cc.	252	47.3	0.17	
Mother liquor	...	368	19.1	1.46	

Per cent K_2O in 3 fractions combined = 54.6 = 86.8 per cent KCl.
Per cent of total K_2O recovered in 3 crystallizations = 88.
Per cent of total I in mother liquor = 87.

By passing the weak liquors over fresh portions of charcoal repeatedly it was found possible to leach out practically all of the potash and iodine with minimum quantities of water.

SUMMARY

1—Comparative laboratory distillations of kelp (*Macrocystis pyrifera*) with oak and fir were made. The data obtained did not indicate that the kelp distillates would have a commercial value.

2—Most of the potash may easily be recovered from the charcoal as a high-grade product.

DIVISION OF AGRICULTURAL CHEMISTRY
CALIFORNIA AGRICULTURAL EXPERIMENT STATION, BERKELEY

NOTE ON IDENTIFYING AMIDO-H-ACIDS

By BERNHARD C. HESSE

Received June 24, 1915

There are no published methods of identifying the 2-amido-H-acid, the 7-amido-H-acid and the 2,7-diamido-H-acid. H-acid is 1,8-amido-naphthol-3,6-disulfo acid. Ability to detect and differentiate these acids is frequently necessary for industrial purposes in obtaining light on the mode of making and the composition of certain coal-tar dyes.

The methods of identification described below were worked out with known H-acid and other materials and were successfully applied to disputed dyes; they are offered with confidence as to accuracy and conclusiveness so far as these three sulfo-acids are concerned. Corresponding mono- and di-amido derivatives of acids isomeric with, or analogous to, H-acid have *not* been similarly examined. Whether conflict exists in that regard has not been determined; this will call for further work by others. This note is not at all a notice of pre-emption but an invitation to others to enter this field. An analysis of the products worked on was not made; reliance for the constitution of these substances is placed solely upon the history and behavior of the materials employed.

The 2-amido-H-acid was made from H-acid by coupling it in hydrochloric solution with diazotized paranitranilin (one molecule), reducing and separating the acid product from the para-phenylene diamine; the 2,7-diamido-H-acid was made from the foregoing coupling product and a further molecule of diazotized paranitranilin, coupling in alkaline (carbonate), solution and treating this result as outlined above; 7-amido-H-acid was made from the coupling product of H-acid and diazotized paranitranilin (one molecule), coupled alkaline (carbonate); this product was reduced and separated as outlined above.

There is nothing new in the coupling methods used. The reducing and separation methods may be new. The general procedure was as follows:

Mix one gram of each of these coupling products with 10 cc. water, heat to 60° C., add one gram zinc dust thoroughly suspended in 5 cc. water, shake thoroughly, add 5 cc. of a 36° Bé. sodium bisulfite solution, shake thoroughly, gradually raise to a boil and maintain at boiling until further color-change does not take place; filter rapidly, cool, add 6 cc. hydrochloric acid (sp. gr. 1.16) to cooled filtrate; cool in a freezing mixture to 0° C. or below and maintain at that temperature until solid no longer separates out (this may take from half hour to 2 or 3 hours); filter upon paper through a Gooch; drain thoroughly; wash carefully with small amounts of saturated salt solution until drip is colorless.